Measurement of Effective Temperatures in an Aging Colloidal Glass

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We study the thermal fluctuations of an optically confined probe particle, suspended in an aging colloidal suspension, as the suspension transforms from a viscous liquid into an elastic glass. The micron-sized bead forms a harmonic oscillator. By monitoring the equal-time fluctuations of the tracer, at two different laser powers, we determine the temperature of the oscillator, $T_{\rm o}$. In the ergodic liquid the temperatures of the oscillator and its environment are equal while, in contrast, in a nonequilibrium glassy phase we find that $T_{\rm o}$ substantially exceeds the bath temperature.

Understanding the slow dynamics of glasses is one of the most fascinating yet difficult challenges in statistical physics. One question which has attracted considerable interest is whether the dynamical fluctuations of a glass can be characterized by a non-equilibrium temperature. A rigorous thermodynamic temperature is strictly impossible to define for an aging glass, which remains far from thermal equilibrium even on long-time scales. Nevertheless various groups [1, 2] have proposed "effective" temperatures with many of the properties expected for an equilibrium temperature. These ideas lead to the surprising prediction of *two* distinct temperatures in an aging glass [1]. The fast rattling modes of particles inside the cage constituted by neighbors thermalize rapidly to the temperature of the environment, $T_{\rm bath}$, while the much slower structural rearrangement of these cages are supposed to be characterized by a second temperature, $T_{\rm eff}$, which mean-field models predict should exceed $T_{\rm bath}$. To date most of the support for this striking two-temperature picture has emerged from simulation results [2] on idealized glasses. Experiments have so far produced conflicting results. Studies of colloidal glasses have reported that $T_{\rm eff}$ increases [3], remains unchanged [4], or even decreases [5] with age in contrast to measurements on structural [6] and spin glasses [7] which have revealed effective temperature warmer than the bath temperature.

In this Letter, we report the temperature of a micrometer-sized sphere immersed in an aging colloidal suspension, as the suspension transforms from a fluid to a glass. The particle, captured in an optical trap, constitutes a microscopic harmonic oscillator whose fluctuations probe the nonequilibrium dynamics of the aging glass. We measure the equal-time fluctuations of this local oscillator and show that, in an ergodic phase, the temperature of the oscillator $T_{\rm o}$ equals the environment temperature $T_{\rm bath}$ of the system, as required by equilibrium statistical mechanics. Significantly, when we repeat the measurements in an aging glass we find a higher temperature and $T_{\rm o} > T_{\rm bath}$.

All experiments to date on colloidal glasses [3, 4, 5] have relied on active, driven measurements. We conduct our experiments instead in a quasi-static limit which has several advantages. First, the experiments are simpler because there is no need to characterize the complete time-dependent response of the system. Second, the lack of an external driving force ensures that we always operate within the linear response regime. We determine the temperature of the laser-trapped particle by recalling that the fluctuations in the coordinate, $\delta x = x - \langle x \rangle$, of an oscillator (with spring constant $k_{\rm T}$), in contact with an equilibrium system at a temperature T, are Gaussian,

$$P(\delta x) = \frac{1}{\sqrt{2\pi T\chi}} \exp\left[-\frac{(\delta x)^2}{2T\chi}\right]. \qquad (1)$$

Here $k_B = 1$ and the static susceptibility χ – the shift in the mean position $\langle x \rangle$ produced by a small constant external field – is simply $1/k_{\rm T}$. Operationally, we define the temperature of the oscillator, $T_{\rm o}$, by the ratio between the one-dimensional mean-squared displacement (MSD) of the probe and the static susceptibility, $T_{\rm o} = \langle \delta x^2 \rangle / \chi$. Equilibrium statistical mechanics guarantees $T_{\rm o} = T$, irrespective of the nature of the coupling between oscillator and system. Out-of-equilibrium however this equivalence no longer holds. Berthier and Barrat [8] have argued that a generalized equipartition principle holds in nonequilibrium glassy materials, implying that an oscillator will record the (slow) effective temperature of a glass. We postpone the interpretation of $T_{\rm o}$ until later and use it, for now, simply as a experimentally accessible measure of the local temperature of a material.

Brownian fluctuations change considerably at the glass transition simply because of elasticity. A fluctuating optically-trapped sphere in an elastic medium, such as a glass, is subject to two harmonic forces; an optical force $F_{\rm opt}$, resulting from the external laser field, and an additional elastic force $F_{\rm e}$, caused by matrix deformation. In an infinite continuum, with shear modulus G and Poisson ratio ν, the elastic force is a linear function of position, $F_{\rm e} = -k_{\rm e}(x - \langle x \rangle)$. The spring constant is $k_{\rm e} = 6\pi GR$ for a sphere of radius R, when $\nu = 1/2$ [9]. The optical forces are $F_{\rm opt} = -k(x - \langle x \rangle)$, with k the optical trap stiffness, so the total spring constant of the trapped particle is $k_{\rm T} = k_{\rm e} + k$. To separate the elastic contribution from the optical contributions to $k_{\rm T}$ we modulate the intensity of the laser beam, rapidly switching it between two levels, which we identify below by the subscripts 1 and 2 respectively. Since $k_{\rm e}$ is independent of laser power,

consecutive measurements of $\langle \delta x^2 \rangle$ at two different laser powers provides estimates of both $k_{\rm e}$ and $T_{\rm o}$,

$$k_{\rm e} = \frac{k_2 \langle \delta x^2 \rangle_2 - k_1 \langle \delta x^2 \rangle_1}{\langle \delta x^2 \rangle_1 - \langle \delta x^2 \rangle_2}$$
$$T_{\rm o} = \frac{(k_2 - k_1) \langle \delta x^2 \rangle_1 \langle \delta x^2 \rangle_2}{\langle \delta x^2 \rangle_1 - \langle \delta x^2 \rangle_2}. \quad (2)$$

Here k_i ($i = 1, 2$) is the optical force constant at each laser power.

The glass studied was a transparent aqueous dispersion of charged colloidal disks of radius $a \approx 15$ nm and 1 nm thick (Laponite RD). The suspension (2.4% mass fraction) was filtered through a 0.45 μm filter to obtain a reproducible initial liquid at $t = 0$. Immediately after filtration, a small amount of a dilute suspension of silica spheres (radius $R = 0.55 \pm 0.03$ μm) was added. A particle was captured in a tightly-focused laser beam ($\lambda = 1064$ nm) and its lateral position, $x(t)$, measured with a quadrant photodetector. The strength of the optical trap was cycled every 52 s between an initial (optical) trap strength, $k_1 = 4.4$ pN/μm, and a final trap strength, $k_2 = 11.0$ pN/μm. All experiments were performed at 22 $\pm$ 1 °C. We confirmed that laser heating was negligible by following the temperature of a trapped silica bead in deionized water. Recording continuously for over an hour at ambient conditions gave a mean temperature of $T_{\rm o} = 300 \pm 8$ K [10], with no upward drift in $T_{\rm o}$. Repeating the measurements on *different* particles showed that the small variation in bead size led to a systematic error in $T_{\rm o}$ of about $\pm$ 40 K.

After mixing the suspension gradually thickens with time and becomes jammed in a glassy state [11]. To identify the point of dynamical arrest we measure the autocorrelation function of the Brownian fluctuations of the probe sphere, $C_{\rm x}(\tau) = \langle \delta x(\tau) \delta x(0) \rangle / \langle \delta x^2 \rangle$. The positional fluctuations are well represented by the stretched exponential relaxation, $C_{\rm x}(\tau) = \exp\left[-(\tau/\tau_\alpha)^\beta\right]$, familiar from generic glassy systems, where τ_α is a terminal relaxation time and β is a stretching exponent. The inset to Fig. 1 reveals that the fitted exponent β varies considerably with age. For $t < t_c$ ($\approx 220 \pm 15$ min) the correlation function is stretched ($\beta < 1$) but with increasing age there is a crossover from a stretched- to a near-exponential form. To decouple changes in the relaxation time from the changes in the exponent β we evaluate the 'mean' relaxation time, $\tau_{\rm m} = (\tau_\alpha/\beta)\Gamma(\beta^{-1})$ where Γ is the gamma function. The relaxation dynamics clearly exhibit two distinct regimes. There is first a fast regime where $\tau_{\rm m}$ grows approximately exponentially with sample age, followed by a second regime of much slower growth where, $\tau_{\rm m} \sim t$. Dynamical arrest occurs at a time t_c which we estimate from the intersection of the corresponding fits in Fig. 1 as 220 $\pm$ 15 min. For $t < t_c$, the system behaves as if it were an ergodic liquid, albeit one with a relaxation time which slows down progressively as t increases. At $t \approx t_c$ the suspension arrests and begins to age.

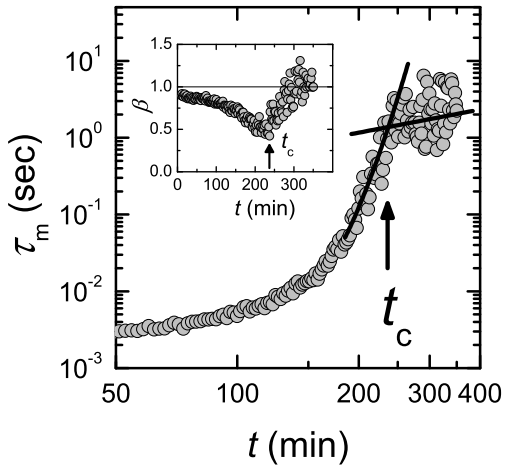

FIG. 1: Variation of the mean relaxation time $\tau_{\rm m}$ with time after preparation for $k_2 = 11.0$ pN/ μm. The correlation function $C_{\rm x}(\tau)$ was fit to a stretched/compressed-exponential relaxation. The continuous lines are fits to the exponential and linear aging regimes respectively. t_c identifies the crossover from exponential to the full aging regime and indicates the approximate position of dynamical arrest. Similar plots are found if the relaxation time is chosen as τ_α or defined as the time at which $C_{\rm x}(\tau)$ has decayed by a factor of $1/e$. Inset: The age dependence of the fitted exponent β.

To explore the effect of the glass transition on the temperature recorded by the Brownian probe, we first examine the probability distribution of the fluctuations, $P(\delta x)$. Fig. 2(a) reveals that although the particle is highly constrained by the glassy matrix, the trajectories exhibit fluctuations which remain Gaussian. This implies that the Einstein expression for the fluctuations (Eq. 1) can be generalized by replacing the bath temperature with an effective temperature. To measure the effective temperature we determine the MSD of the trapped particle, recognizing that the dramatic dynamical slowing at the glass transition, evident in Fig 1, requires care if the asymptotic limit is to be evaluated. To check for convergence, we split each recorded 52 s particle trajectory into a number of shorter equal-time lengths of duration t_B and evaluate the MSD of each, before averaging the values together. We choose $t_B = 3.3$ s in order to have a good signal to noise ratio whilst retaining many long-lived fluctuations. The elastic modulus G of a (hard-sphere) repulsive glass scales as $G \sim k_B T/a^3$, where a is the radius of the particles that form the glass, so the thermal fluctuations of a sphere of radius R embedded in a glass are restricted to a cage with a characteristic size of $l_g \sim (a^3/R)^{1/2}$ [9, 12]. Taking the effective radius as $a \approx 45$ nm [13] yields $l_g^2 \approx 200$ nm^2 for our system. Consistent with this picture the asymptotic MSD exhibits two distinct regimes. Fig. 2(b) demonstrates that for

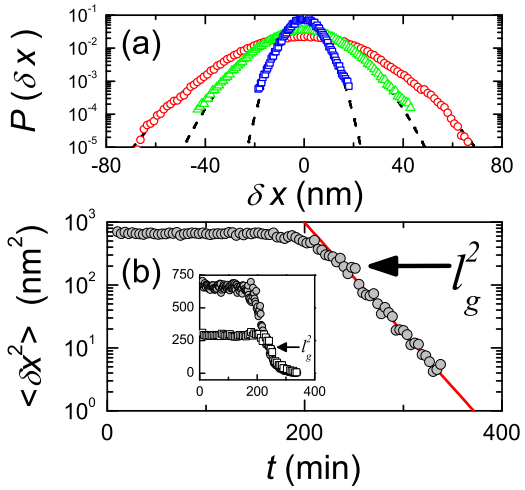

FIG. 2: (color online). (a) Probability distributions of the fluctuations of probe particles for different times after preparation, $t = 200$ min (circles), 250 min (triangles), and 301 min (squares). The dashed lines are Gaussian fits to the data. (b) Asymptotic mean-square displacement (MSD) of probe, confined in an optical trap of strength $k_1 = 4.4$ pN/μm, as a function of sample age t. The statistical errors are of order ± 11 nm^2. The arrow indicates the square of the localization length in the glass, l_g^2. The solid line is an exponential fit to the MSD within the glass. The inset depicts a linear plot of the MSD (in nm^2) as function of age, in weak (k_1: circles) and strong (k_2: squares) laser traps. $k_2 = 11.0$ pN/μm. Note the MSDs are identical, within error, for $t \gtrsim 250$ min where $\langle \delta x^2 \rangle \lesssim l_g^2$.

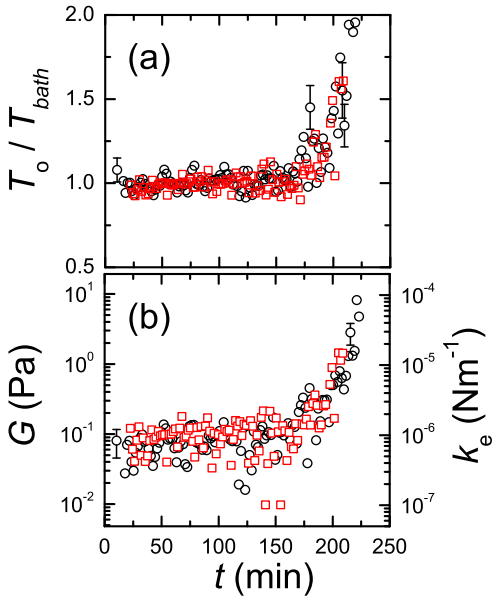

FIG. 3: (color online) (a) Effective temperature as a function of sample age. The circles and squares depict the results of measurements using similarly-sized particles in two physically-distinct laponite samples. The scatter illustrates the typical level of reproducibility achieved. Errors bars, which are estimated from the variability in $\langle \delta x^2 \rangle$ for $t < 100$ min where the MSD is constant, are only shown on a few representative points for clarity. (b) Age dependence of the single particle elastic spring constant k_e and the equivalent elastic modulus $G = k_e/6\pi R$.

$t \lesssim 100$ min, where $\langle \delta x^2 \rangle > l_g^2$, the degree of localization does not change with age although it depends sensitively on the laser intensity, as expected for confinement by an external field. With increasing age, by contrast, the asymptotic MSD shows a progressively weaker dependence on intensity. Indeed when $\langle \delta x^2 \rangle \approx l_g^2$ the thermal fluctuations are almost totally independent of the laser field, consistent with permanent caging of the probe particle by the glass. The localization length in the glass shrinks exponentially as the glass get older, until at very long times ($t \simeq 350$ min) all measurable motion ceases.

The change in localization with time, evident in Fig. 2(b), allows us to monitor the temperature of the slow structural modes of the glass. Figure 3 shows the age dependence of the oscillator temperature T_o and the shear modulus G, calculated from Eq. 2 and the data of Fig. 2(b) (assuming $\nu = 0.5$). The data reveals a marked increase in T_o approaching the liquid-glass transition. For $t \ll t_c$ the temperature of the Brownian probe is approximately constant at 247 ± 20 K [10], which given that the systematic uncertainty in T_o is at least 40K, is in reasonable agreement with the environment temperature, $T_{\rm bath} = 295$ K. By contrast, in the glass we find a systematic increase in the oscillator temperature with increasing age, with the ratio $T_o/T_{\rm bath} \approx 2$ at the longest accessible age. Since the glass is non-ergodic an ensemble average quantity such as the effective temperature strictly requires an average over many probe particles. To verify the reproducibility of our results we repeated measurements using similarly-sized particles in different physical samples with the same nominal laponite concentration and found no significant difference in the age dependence of $T_o/T_{\rm bath}$. An example of the data spread for data sets recorded from two different samples is shown in Fig. 3(a). We attribute this homogeneity to the fact that the probe is significantly larger than the laponite particles.

The growth evident in T_o as the glass ages is, at first sight, very surprising. Intuitively, one expects a glass to cool as it ages and $T_{\rm eff}$ to fall with increasing t. To account for the temperature increase, we analyze a simple stochastic model of our experiments, ignoring the detailed microhydrodynamic coupling between the fluctuations of the embedded probe and the sea of platelets. The model, introduced in [14], considers the diffusion of a harmonically-bound particle coupled to two thermal baths. The two baths are kept at different temperatures to mimic the effects of the *fast* and *slow* modes of the glass on probe diffusion. The fast bath is held at a tem-

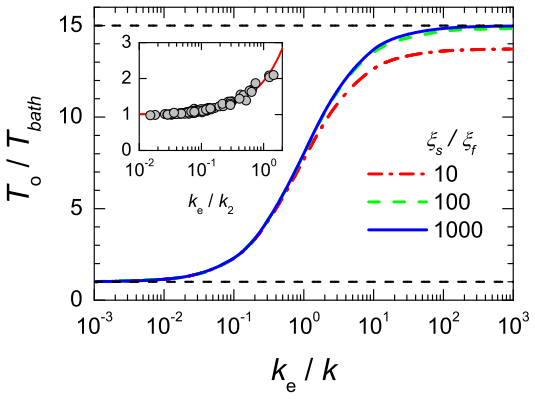

FIG. 4: (color online) Elasticity dependence of the scaled oscillator temperature for $T_{\rm eff} = 15T_{\rm bath}$. The solid lines are obtained from the analytic solution of Eq. 3 for relative timescales $\xi_s/\xi_f = 10$ (red), 100 (green), and 1000 (blue). Inset: Experimental dependence of $T_{\rm o}/T_{\rm bath}$ on the elasticity ratio, $k_{\rm e}/k_2$ (circles). The continuous line depict the theoretical predictions for $\xi_s/\xi_f = 100$.

perature $T_{\rm bath}$ and exerts an instantaneous friction of $\xi_f\dot{x}(t)$ on the particle while the second, slower bath is maintained at a (higher) temperature $T_{\rm eff}$ and is associated with the memory function, $\Gamma(t)$. In the overdamped limit, where acceleration can be neglected, Brownian diffusion is governed by the generalized Langevin equation,

$$kx(t) = -\int_0^t d\tau\Gamma(t-\tau)\dot{x}(\tau) - \xi_f\dot{x}(t) + \theta(t) + \gamma(t). \quad (3)$$

The random forces due to the fast bath are Gaussian with $\langle\gamma(t)\rangle = 0$ and $\langle\gamma(t)\gamma(\tau)\rangle = 2\xi_f T_{\rm bath}\delta(t-\tau)$, whereas the slow bath is characterized by $\langle\theta(t)\theta(\tau)\rangle = T_{\rm eff}\Gamma(t-\tau)$. Approximating the glass by a Maxwell fluid, with zero shear viscosity η_s and shear modulus G, the retarded friction on a sphere of radius R is $\Gamma(t) = k_{\rm e}\exp(-k_{\rm e}t/\xi_s)$, with $k_{\rm e} = 6\pi GR$ and $\xi_s = 6\pi\eta_s R$ [15]. Following Ref. [14], an analytic expression may be written down for the reduced oscillator temperature $\widetilde{T} = T_{\rm o}/T_{\rm bath}$. Fig. 4 shows the dependence of the oscillator temperature on the elasticity ratio $k_{\rm e}/k$. Clearly while the oscillator temperature always lies between the temperatures of the fast and slow baths, the exact value is sharply dependent on $k_{\rm e}/k$. Only for $k_{\rm e} \gg k$ does $T_{\rm o}$ approach the temperature of the slow bath. Plotting the experimental data for $\widetilde{T}$ as a function of $k_{\rm e}/k_2$ reveals a very similar trend (shown in the inset of Fig. 4). Consequently we attribute the increase in the measured temperature with age to the growing strength of the mechanical coupling between particle and glass.

In summary, we have measured the quasi-static fluctuations of an optically-bound probe particle immersed in an aging glass. Using a generalized equipartition principle we determine the temperature of the oscillator formed by the trapped probe. In a glass we find an oscillator temperature which is substantially higher than the temperature of the environment; while in the fluid the temperatures of the oscillator and environment are essentially equal. We propose a simple theoretical model for these nonequilibrium experiments which reveals that, at high elasticities, the probe thermalizes to the effective temperature of the slow modes of the glass. Our findings agree broadly with the results obtained recently by Abou *et al.* and Strachan *et al.* [3], who used different techniques to measure $T_{\rm eff}$. Taken together this agreement provides strong experimental confirmation for the existence of an elevated effective temperature in a glass. Future work will look at using comparably-sized probe and glass particles to study the role of dynamical heterogeneities on the effective temperature.

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